Effect of Processing on Morphological Structure of Polyacrylonitrile Matrix Nano-ZnO Composites

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Received 17 July 2002; accepted 20 February 2003

ABSTRACT: The effects of processing methods—free casting and spinning—on dispersion of nano-ZnO in a polyacrylonitrile (PAN) matrix were studied for this article. From observation with an transmission electron microscope, it was found that monoaxial drawing in spinning processing formed a fiberlike image of the nano-ZnO phase in the PAN matrix. The geometric parameters—the diameter and ratio of the nanoparticle phase—were about 20 and 15 nm, respectively, when the concentration of nano-ZnO was 1 wt % in the PAN matrix, whereas spherelike morphology was obtained by free casting, for which, naturally, the ratio of its length to its diameter was unity. This indicates that evidently the morphology of the nanoparticle phase is affected by processing methods. However, when the concentration of nano-ZnO went up to 2 wt % in the PAN matrix spinning process, the linear ratio of length to diameter of the nanoparticle phase decreased to 2.9 because drawing energy adsorption, through deformation of the nanoparticle phase, became a marked effect. The degree of anisotropy, including crystallization and orientation of polymer, was also affected by the concentration of nano-ZnO for the same reason. When the concentration of nano-ZnO reached 2 wt %, the anisotropy of PAN was obviously depressed according to the results of wide-angle X-ray measurement. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1053–1057, 2003

Key words: processing; polyacrylonitrile; nano; zinc oxide; morphology

INTRODUCTION

In most cases, the processing of polymers determines a material's structure and properties. For polymeric matrix composites, this characteristic is more important because the related morphology is a key factor in its physical and mechanical properties.

Many articles have elucidated the preparation of nanoparticles of metals and synthetic ceramics,[1–3] and even for their composites, innumerable articles have appeared in polymer-related journals.[4–8] The reason for all this research has been to obtain particular optical, electronic, and catalytic properties. These properties have size-dependent characteristics at the nano level. Here, as is known, the properties of both matrices and nanoparticles are important. Polymers are very important matrices because of their flexibility and easy processing. Nanoparticles impart composite materials with functional properties or improved mechanical properties. Therefore, assembly of these composite materials is the key to success. For these reasons, researchers sometimes have tried to find special ways for special systems.[4–8] Few investigators have previously directly tried fundamental methods, such as extruding and spinning. Generally, these basic methods are very attractive for their low cost and widely available equipment. Some interesting attempts,[9] in which nanoparticles were dispersed in a polymer matrix by traditional methods with additional means of assistance, suggest other possibilities. For example, the use of ultrasonics is a good way of assisting the dispersion of nanoparticles in a polymer matrix. In addition to investigating methodology, it is important to try to know how processing affects the morphological structures of composites. The choice of a popular polymer and nanoparticle matrix—polyacrylonitrile and zinc oxide— for this study makes this work more meaningful for practical applications.

In this study we tried two techniques, both the free-cast and spinning processing methods, as examples. The processing principles of these methods are extremely different. For free casting, composite films are gained in a free-flow state, in which there is an extremely slight shearing stress. For the spinning method, spun composite filaments are obtained by a typically one-dimensional drawing. Knowing the relationship between preparation and morphological structure was helpful in understanding the mechanisms and effective factors of the

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Contract grant sponsors: National Natural Scientific Foundation of People's Republic of China and Qingdao Municipal Scientific and Technological Committee.

Journal of Applied Polymer Science, Vol. 90, 1053–1057 (2003)

structural formation of the nanoparticle composites in these processes.

EXPERIMENTAL

Raw materials

Reagents used in this study were urea, ammonia, zinc acetate, and *N,N*-dimethylformamide (DMF), which were used without further pretreatment. Commercial-grade polyacrylonitrile (PAN), which is a copolymer composed of 93% acrylonitrile, 6% methacrylate, and 1% sodium acrylate, was supplied by Zibo Synthetic Fiber Company, Zibo, Shandong, People's Republic of China.

Preparation of samples

Nano–zinc oxide was according to the following reactions:

$$CO(NH_2)_2 + 3H_2O \rightarrow CO_2 + 2NH_3 \cdot H_2O \quad (1)$$

$$Zn^{2+} + 2NH_3 \cdot H_2O \rightarrow Zn(OH)_2 + 2NH_4^{+} \quad (2)$$

$$Zn(OH)_2 \rightarrow ZnO + 2H_2O \quad (3)$$

Aqueous solutions of Zn^{2+} and urea were added into a flask with rapid agitation. The molar ratio of Zn^{2+} to urea was about 1:9. For reactions 1 and 2 the temperature in the flask was maintained at 95°C ± 2°C for 2–2.5 h, but for reaction 3 the temperature was in the range of 220°C–450°C. After reaction the products were added into distilled water and agitated for 20 min and were filtered under vacuum. This washing process was repeated twice. Then the samples were washed twice with ethanol in the same conditions. After drying, the samples were nano–zinc oxide (ZnO) with diameters of 20–35 nm. Because nanoparticles are easy to agglomerate into larger-size congeries because of their high surface energy, we gave the samples a surface passivation treatment. This nano-ZnO was added to a silver ion–containing solution of surfactant $C_{18}H_{37}O(CH_2CH_2O)_{10}H$ and was agitated for 2 h. After filtration and drying under vacuum, the final product was designated as nanosurface-passivated ZnO (nano-SPZnO).

For an ideal dispersion of nanoparticles in the PAN solution, the nanoparticle suspensions in DMF first were vibrated by ultrasonics at 60°C for 1 h. Then the weighed PAN was added to this flask at 80°C. After 2 h of agitation the solutions were cast on a clean glass plate. The cast films were predried at ambient temperature for 4 h and then were heated to 80°C for 2 h in an oven. The thickness of the final film was about 500 μm.

The spinning fluids consisted of 20 wt % PAN with 0, 1, and 2 wt % nanoparticles, in different spinning experiments. At 60°C these solutions were pumped into and extruded out of a spinneret having 40 apertures, each of which had a diameter of 0.06 mm. The spinning device used in this experiment was a horizontal device self-made at Dong-Hua University, Shanghai, People's Republic of China. The front face of the spinneret was almost vertical, and the filaments were transferred almost horizontally through a 10°C–15°C spinning bath that was 20 wt % DMF and 80 wt % H_2O. The filaments coagulated by the dual diffusion principle of DMF-out-of and H_2O-into the filaments. After going through the spinning bath, the filaments were immersed in an extraction bath to be washed at 60°C, and then they were drawn in boiling water. The total draw ratio of the filaments in spinning and drawing was 8 times, relative to the extruded length at spinneret. Finally, the drawn filaments were rewound on a roller, and the rollers with filaments were dipped in distilled water for 2 h before they were dried.

Measurements

Transmission electron microscopy (TEM) measurements were performed with a JEM-2000EX (Tachikawa, Tokyo, Japan) operated at 160–200 KV. The filament samples were embedded in wax and were cut with a slicer (Dupont MT-6000 microtome; Sorvall Instruments, DE). The wide-angle X-ray diffraction study was done on a Bruker-AXS D8 (Bruker AXS, Inc., Madison, WI). The filaments used in measurement were extended and bonded on a frame.

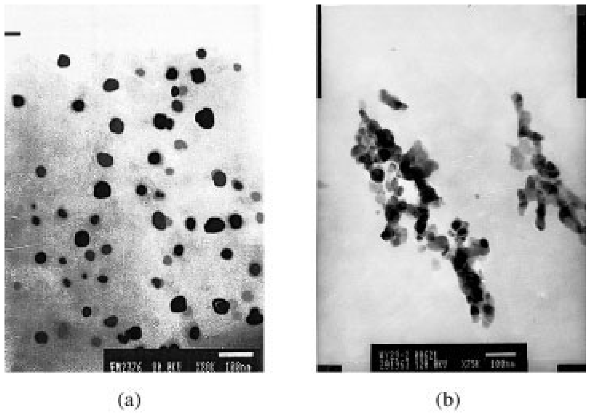
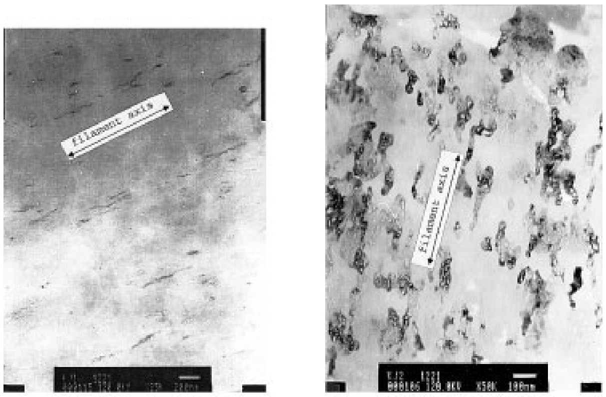

(a) (b)

Figure 1 TEM images of free-cast samples of PAN matrix nanocomposites: (a) 2 wt % nano-SPZnO (scale bar in bottom black rectangle represents 100 nm; black dots are nano-SPZnO particles); (b) 2 wt % nano-ZnO (scale bar in bottom black rectangle represents 100 nm; black dots are nano-ZnO phase).



(a) (b)

Figure 2 TEM images of spun samples of PAN matrix nanocomposites: (a) 1 wt % nano-SPZnO; (scale bar in bottom black rectangle represents 200 nm; arrow shows filament drawing direction; black line traces is lined-up nanoparticle phase); (b) 2 wt % nano-SPZnO (scale bar in bottom black rectangle represents 100 nm; arrow shows filament drawing direction; black slim image is nanoparticle phase, linearly stretched up by filament drawing).

RESULTS AND DISCUSSION

Dispersion of nanoparticles in PAN matrix

Free cast

The free-cast composite samples of nano-SPZnO and nano-ZnO particles in the PAN matrix were examined by transmission electron microscopy (TEM). The images are shown in Figure 1(a,b). Both show a well-dispersed morphology. It is obvious that ultrasonic energy is helpful in dispersing these nanoparticles in the PAN matrix before casting. Although the method of ultrasonic-assisted dispersion of nanoparticles in polymer matrices has been mentioned in the literature,[9] there has been little information about the relationship between ultrasonic assistance and the morphology of related nanocomposites. The results shown in Figure 1 help to show this relationship: the differences between the two images are obvious. Figure 1(a) shows that nano-SPZnO particles in the PAN matrix are separated and that most particles have a diameter of 50–80 nm. It confirms that surface treatment was helpful for the dispersion of the nanoparticles in the polymer matrix. On the other hand, surface treatment also caused the diameters of the nanoparticles to increase. In Figure 1(b) smaller diameters, of about 25–35 nm, for single particles can be found easily when the nanoparticles are not surface treated. But most nanoparticles agglomerate. That means that surface treatment should be necessary to obtain a morphology of well-separated nanoparticles in a PAN matrix.

Spinning

Figure 2 shows the morphology of PAN–nano-SPZnO filaments spun by the wet spinning process. The concentrations of nano-SPZnO in PAN shown in Figure 2(a,b) are 1 and 2 wt %, respectively. The geometrical parameters of dispersed nanoparticle phases are listed in Table I. For 1 wt % nano-SPZnO, shown in Figure 2(a), the individual diameters of the nanoparticle phase are around 20 nm, and the linear phase length is about 300 nm at most, making the ratio of linear length to diameter about 15:1. Correspondingly, for 2 wt % nano-SPZnO, shown in Figure 2(b), the diameter and the linear length are about 35 and 100 nm at most, respectively; thus, the rough ratio of linear length to diameter is 2.9:1. All the data mentioned above suggest that the fiberlike linear morphology of nano-SPZnO phases in PAN matrix was formed through spinning processing, instead of having the pseudo-spherical morphology shown in Figure 1. Obviously, the extension of the nanoparticle phase was driven by the drawing stress along the filament axis, which is transferred by the PAN matrix. In other words, the array of nanoparticles was obviously influenced by the drawing deformation of the filaments. It is noteworthy that the ratio of length to diameter of the nano-SPZnO phase decreased with an increase in the concentration of nano-SPZnO in the PAN matrix from 15:1 at 1 wt %, 5 times larger than the 2.9:1 ratio at 2 wt %.

TABLE I
Evaluated Geometrical Parameters of Nanoparticle Phases in PAN Matrix Filaments

		Free cast			Spinning		
Content of nanoparticles	Nanoparticle and figure number	Diameter (D, nm)	Linear length (L, nm)	Ratio of L to D	Diameter (D, nm)	Linear length (L, nm)	Ratio of L to D
2%wt	Nano SPZnO, Figure 1(a)	50–80	50–80	1			
2%wt	Nano ZnO, Fig. 1(b)	25–35	25–35	1[a]			
1%wt	Nano SPZnO, Figure 2(a)				~20	~300	~15
2%wt	Nano SPZnO, Figure 2(b)				~35	~100	~2.9

[a] Here, the ratio of L to D is only for single particles, not for the evaluation of particle conglomeration.

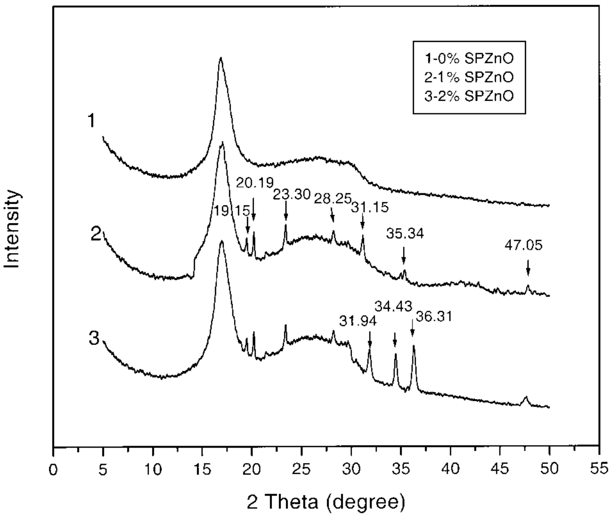


Figure 3 X-ray diffraction patterns of PAN matrix nano-SPZnO composite films by free casting. Curves 1, 2, and 3 correspond to PAN, 1 wt % nano-SPZnO, and 2 wt % nano-SPZnO.

Effect of nanoparticles on anisotropy of PAN matrix

Free cast

In general, although PAN does not have a clear dimension of *c* in its unit cell, its highly ordered macromolecular arrangement is still called crystallization.[10] Figure 3 shows X-ray diffraction patterns (XRD) of free-cast samples. Curves 1, 2, and 3 refer to 0 (pure PAN), 1 and 2 wt % nano-SPZnO contents in PAN matrix, respectively. The XRD pattern of pure PAN shows a sharp crystalline peak (16.8°) and a broad noncrystalline peak (22°–32°) [Fig. 3(1)]. The characteristic peak at 16.80 corresponds to the orthorhombic PAN (110) reflection.[11] As shown in Figure 3(2), there are six other peaks, at 2θ = 19.15°, 20.19°, 23.30°, 28.25°, 31.15°, and 35.34°, which correspond to the nano-SPZnO phase.[12] In curve 3 of Figure 3, the peaks at 2θ = 23.30°, 31.94°, and 34.43° are also the characteristic diffractions of nano-SPZnO. As for the peaks at 36.31° and 47.05° in curves 2 and 3 of Figure 3, they relate to silver crystals from surface passivation.[12] All these results show that these composite samples consisted of polyacrylonitrile and nano-SPZnO nanoparticle phases.

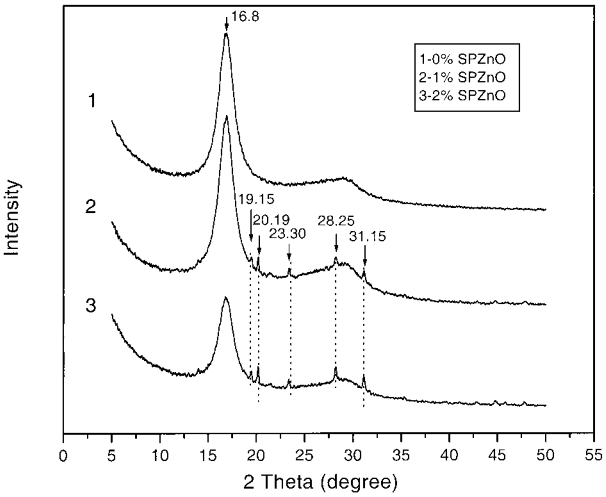


Figure 4 X-ray diffraction patterns of PAN matrix nano-SPZnO composite filaments. Curve 1, 2, and 3 are 0, 1, and 2 wt % nano-SPZnO.

As free-cast samples, their quantitative degrees of crystallization can be evaluated, according to the traditional way, by Hindeleh's equation as follows[13]:

$$C = Sc/St = Sc/(Sa + Sc) \times 100\% \qquad (4)$$

where C is the degree (%) of crystallization, Sc is the peak area, and St is the total area under the diffraction curve. For the curves in Figure 3, the evaluated data are listed in Table II. The results show that an increase in nanoparticle concentration caused a small increase in the total degree of crystallization, whereas the crystallization degree of the PAN matrix at 2θ = 16.8° did not show an obvious change. Even though there are small differences among the degree of crystallization values of the PAN matrices listed in Table II, the differences are within the errors of the calculation method. So, it is reasonable to ascribe the increase in total crystallization degree of the samples to crystallization of the nanoparticles.

Spinning

The spinning formation of the composites was different from free casting. Figure 4 shows the X-ray diffraction patterns of spun samples, which contained 0 (plain PAN), 1, and 2 wt % nano-SPZnO particles. The

TABLE II
Effect of Nanoparticle Content in PAN Matrix on Crystallization by Free Casting

Nanoparticle content in PAN film (% wt)	Total crystallization degree (%)	PAN crystallization degree at 2θ = 16.8° (%)
0	9.89	9.89
1	10.54	9.13
2	11.63	9.45

curves in Figure 4 are very similar to those in Figure 3. They show sharp peaks at 16.8°, broad peaks ranging from 20° to 32°, and sharp and small peaks relating to ZnO crystals. Therefore, for spun composite filaments, the composites contained both polyacrylonitrile crystalline and nano-SPZnO crystalline phases. Unfortunately, we could not determine the degree of crystallization simply using Hindeleh's method because of the sample's anisotropy including both crystallization and orientation of polymer chains.[14,15] However, we could evaluate the effect of nanoparticles on the superstructure of polymer matrix based on Figure 4. The change in the relative peak strength of crystalline polyacrylonitrile at 16.8° to a broad noncrystalline region is reasonable evidence of this. The upper two curves in Figure 4, which look similar, are for plain PAN and the sample containing 1 wt % nano-SPZnO particles, whereas the bottom one, for 2 wt % nano-SPZnO, has a much smaller peak at 16.8° and a bigger broad peak for noncrystalline PAN. This means that the nanoparticles depressed the anisotropy of polyacrylonitrile and enhanced the amorphous content when its concentration reached a critical value (for example, 2 wt %). As is known, anisotropy is from the drawing energy in fiber formation. Its depression indicates that the drawing energy was absorbed for some reason. We suppose that the higher concentration of nano-SPZnO particles produced a higher specific interface between the nano-SPZnO particles and the polymer matrix. In the drawing process this interface absorbed drawing energy and caused the linear array of nano-SPZnO particles (in Fig. 2). This suggested scenario is in accord with the image change shown in Figure 2(a,b).

CONCLUSIONS

The significance of this study is that traditional polymer processing methods, free casting and spinning, were used in polymer–matrix nanocomposite preparations. Unique polyacrylonitrile solutions including nano-ZnO and nano-SPZnO particles were prepared with the sole assistance of ultrasonic vibration.

The samples obtained from free casting and spinning were analyzed by transmission electron microscopy and X-ray diffraction. The results of sample analyses indicated that the methods were effective. TEM results revealed the differences in morphologies of the free-casting and spinning processes. For free-cast samples, the image of the nanoparticle phase was spherelike, with diameters of 25–35 nm for nano-ZnO and 50 – 80 nm for nano-SPZnO (Fig. 1). However, with the spinning process fiberlike regions of nanoparticle phase were formed, with their geometrical sizes changing with the concentration of nanoparticles. A diameter of 20 nm with a ratio of length to diameter of about 15:1 were obtained at 1 wt % nano-SPZnO, whereas at 2 wt % content the corresponding parameters were about 35 and 2.9, respectively. X-ray data showed that for free casting the addition of nanoparticles (i.e., nano-ZnO and nano-SPZnO) had little influence on the crystallization of the polyacrylonitrile matrix, whereas for spinning these nanoparticles depressed the anisotropy of the polymer matrix.

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